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# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 06184943  
PUBLICATION DATE : 05-07-94

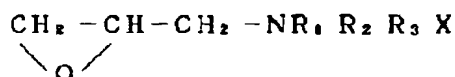
APPLICATION DATE : 18-12-92  
APPLICATION NUMBER : 04356086

APPLICANT : SHIN ETSU CHEM CO LTD;

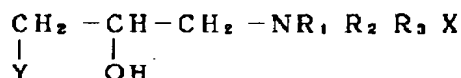
INVENTOR : NAGURA SHIGEHIO;

INT.CL. : D06M 15/03

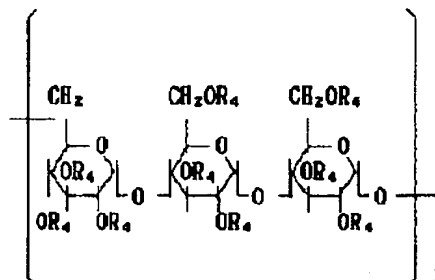
TITLE : ANTISTATIC SIZING AGENT FOR FIBER



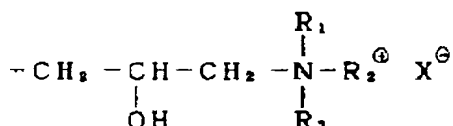
I



II



III



IV

**ABSTRACT :** **PURPOSE:** To obtain an antistatic sizing agent for fiber, comprising a cationized pullulan, excellent in antistatic effects at a low humidity without discoloring fiber, good in hand and capable of manifesting excellent sizing effects without causing the deterioration in color fastness.

**CONSTITUTION:** A raw material pullulan is made to react with a cationizing agent selected from formulas I and II ( $\text{R}_1$  to  $\text{R}_3$  are hydrocarbon; X and Y are halogen) to provide a cationized pullulan, expressed by formula III [ $\text{R}_4$  is H or substituent group expressed by formula IV; n is 20-20000; ( $\text{R}_1$  to  $\text{R}_3$  are hydrocarbon,  $\text{R}_1$  and  $\text{R}_2$  are preferably 1-3C alkyl;  $\text{R}_3$  is 1-18C alkyl; X is halogen, especially chlorine)] and having preferably a substituent group, expressed by formula IV and present in an amount of  $\geq 0.01$  expressed in terms of the degree of substitution based on the anhydroglucose unit. The resultant cationized pullulan is then used as a substrate and a cationic surfactant, as necessary, is added thereto. A textile material such as natural or synthetic fiber is subsequently immersed and treated with the prepared treating solution to afford the objective antistatic sizing agent capable of assuming excellent sizing effects. Trimethylammonium chloride, dimethyloctylammonium chloride, etc., can be exemplified as a common part of  $\text{NR}_1\text{R}_2\text{R}_3\text{X}$  expressed by formulas I and II.

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# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **SHIN ETSU CHEM CO LTD**

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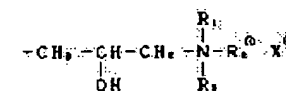
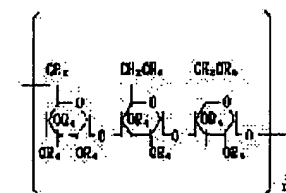
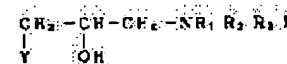
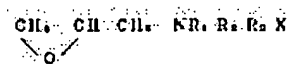
(72)Inventor : **NARITA MITSUO  
NAGURA SHIGEHIRO**

## (54) ANTISTATIC SIZING AGENT FOR FIBER

### (57)Abstract:

PURPOSE: To obtain an antistatic sizing agent for fiber, comprising a cationized pullulan, excellent in antistatic effects at a low humidity without discoloring fiber, good in hand and capable of manifesting excellent sizing effects without causing the deterioration in color fastness.

CONSTITUTION: A raw material pullulan is made to react with a cationizing agent selected from formulas I and II (R1 to R3 are hydrocarbon; X and Y are halogen) to provide a cationized pullulan, expressed by formula III [R4 is H or substituent group expressed by formula IV; n is 20-20000; (R1 to R3 are hydrocarbon, R1 and R2 are preferably 1-3C alkyl; R3 is 1-18C alkyl; X is halogen, especially chlorine)] and having preferably a substituent group, expressed by formula IV and present in an amount of >0.01 expressed in terms of the degree of substitution based on the anhydroglucose unit. The resultant cationized pullulan is then used as a substrate and a cationic surfactant, as necessary, is added thereto. A textile material such as natural or synthetic fiber is subsequently immersed and treated with the prepared treating solution to afford the objective antistatic sizing agent capable of assuming excellent sizing effects. Trimethylammonium chloride, dimethyloctylammonium chloride, etc., can be exemplified as a common part of NR1R2R3X expressed by formulas I and II.



## LEGAL STATUS

[Date of request for examination]

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 CLAIMS
 

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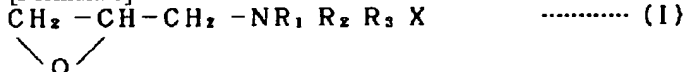
[Claim(s)]

[Claim 1] The antistatic sizing agent for fiber characterized by containing a cation-ized pullulan.

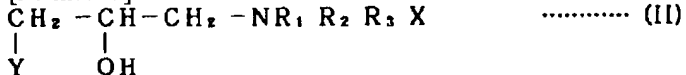
[Claim 2] The antistatic sizing agent for fiber characterized by containing a cation nature surfactant for a cation-ized pullulan two to 12% of the weight 0.005 to 5% of the weight.

[Claim 3] The compound [above-mentioned general formula expressed with the compound and the general formula (II), and (\*\* 2) which are expressed with a general formula (I) and (\*\* 1) in a pullulan (I), It sets to (II) and is R1, R2, and R3. Hydrocarbon group, X and Y are the antistatic sizing agent for fiber of the claims 1 or 2 characterized by containing the cation-ized pullulan obtained by [ of the cation-ized agent chosen from the group which consists of halogen atom] ] making it react more than with a kind at least.

[Formula 1]



[Formula 2]




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[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention has the antistatic nature in the outstanding sizing effect and outstanding low humidity in more detail about the antistatic sizing agent for fiber, and it relates to the antistatic sizing agent for fiber from which good feeling is obtained, without making fiber discolor further.

[0002]

[Description of the Prior Art] The antistatic agent for synthetic fibers using the cation-ized cellulose, cation-ized starch, or chitosan currently indicated as a conventional antistatic agent for fiber by the new fourth class compound and JP,57-82576,A which are indicated by JP,51-63104,A is known. Furthermore, as the fiber softening agent constituent of JP,52-132193,A which made the cation activator and the cation denaturation cellulose the principal component, and a thickening agent, the home thickening-agent constituent of JP,53-94688,A is known as a softening agent.

[0003]

[Problem(s) to be Solved by the Invention] however, the thing which is repeated and done for the flexible processing of the product according to such conventional technology -- fiber -- yellowing -- it gray-ized and the fall of colorfastness was able to give Moreover, the antistatic effect in the flare intensity and the degree of low temperature of sizing is inadequate, a not good trouble also has a hand, and these solutions were desired.

[0004] Therefore, especially the purpose of this invention is to offer the antistatic sizing agent which presents the sizing effect which hardly has hygroscopicity, and was not made to discolor a more effective antistatic sizing agent, i.e., fiber, to the high synthetic fiber of electrification nature to fiber, but maintained colorfastness, was excellent in the antistatic nature in low humidity, and was excellent, without spoiling good feeling.

[0005]

[Means for Solving the Problem] Especially this invention persons repeated the examination to the film physical properties which a pullulan derivative has. Consequently, the knowledge of the ability to fully obtain an above-mentioned function was carried out by making a cation-ized pullulan into a basis or using a cation nature surfactant together further.

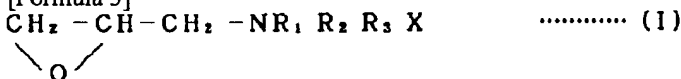
[0006] The antistatic sizing agent for fiber of a claim 1 is characterized by containing a cation-ized pullulan for the above-mentioned purpose achievement.

[0007] The antistatic sizing agent for fiber of a claim 2 is characterized by containing a cation nature surfactant for a cation-ized pullulan two to 12% of the weight 0.005 to 5% of the weight for the above-mentioned purpose achievement.

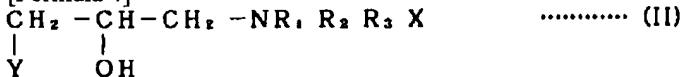
[0008] Invention of a claim 3 is set to the antistatic sizing agent for fiber of claims 1 or 2 for the above-mentioned purpose achievement. The compound [above-mentioned general formula expressed with the compound and the general formula (II), and (\*\* 4) which are expressed with a general formula (I) and (\*\* 3) in a pullulan (I), It sets to (II) and is R1, R2, and R3. It is characterized by a hydrocarbon group, and X and Y containing the cation-ized pullulan obtained by [ of the cation-ized agent chosen from the group which consists of halogen atom ] making it react more than with a kind at least.

[0009]

[Formula 3]



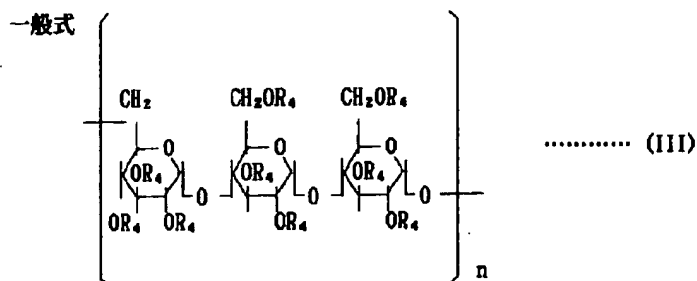
[Formula 4]



[0010] The antistatic sizing agent for fiber concerning this invention is characterized by containing as a basis the cation-ized pullulan expressed with the following general formula (III).

[0011]

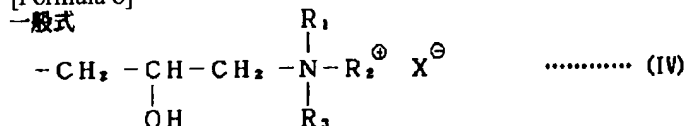
[Formula 5]



[0012] However, inside R<sub>4</sub> of the above-mentioned formula It responds to the degree of substitution of the cation-ized pullulan which is a hydrogen atom or the substituent expressed with the following general formula (IV), and is obtained, and the above-mentioned substituent is R<sub>4</sub>. The existing hydrogen atom is replaced.

[0013]

[Formula 6]



[0014] The above-mentioned substituent originates in a cation-ized agent, and is R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>. It is R<sub>1</sub> and R<sub>2</sub> so that a hydrocarbon group may be expressed and it may mention later about a cation-ized agent. The alkyl group of carbon numbers 1-3 is desirable, and it is R<sub>3</sub>. The alkyl group of carbon numbers 1-18 is desirable.

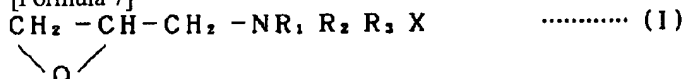
[0015] X -- chlorine and SHUU -- it is halogen atoms, such as base and iodine, and it is desirable that it is chlorine Moreover, in a general formula (III), n is usually 20-20,000.

[0016] As for the substituent expressed with a general formula (IV), it is desirable that the 0.1 per [ this unit / more than ] thing which 0.01 or more [ per anhydrous glucose unit ] exist as a degree of average substitution exists desirable still more preferably. Properties, such as moistness required of the less than 0.01 degree of substitution when it uses as a basis of an antistatic sizing agent, in order to operate enough the distributed homogeneity at the time of using a product for flexible processing and antistatic, may be unable to be given, and it is not desirable.

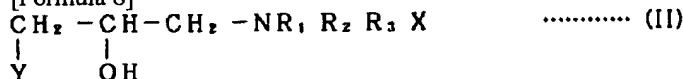
[0017] In this invention, the cation-ized pullulan used as a basis for antistatic sizing agents for fiber The compound [above-mentioned general formula expressed with the compound, the general formula (II), and (\*\* 8) which are expressed with a general formula (I) and (\*\* 7) to a raw material pullulan under existence of water and the alkaline matter (I), It sets to (II) and is R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>. A hydrocarbon group, and X and Y can be obtained by [ of the cation-ized agent chosen from the group which consists of halogen atom ] making it react more than with a kind at least.

[0018]

[Formula 7]



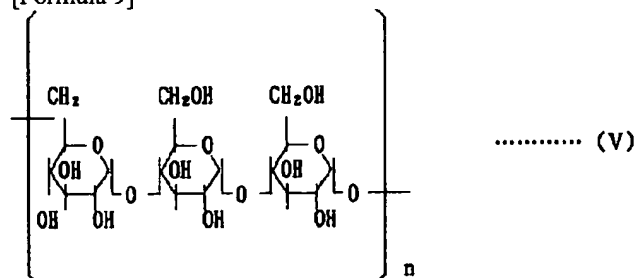
[Formula 8]



[0019] The above-mentioned raw material pullulan makes a unit the maltotriose which is the trimer of a glucose like a general formula (V) and (\*\* 9), and this trimer is alpha-1 which is a different combination, and a linear polymer which carried out repetitive combination by six combination. As molecular weight of a pullulan, 10,000-10 million are 100,000-10 million desirable still more preferably. Therefore, the inside n of (a general formula V) is usually 20-20,000.

[0020]

[Formula 9]



[0021] Especially a limit does not have a raw material pullulan in the manufacture method. For example, \*\*\*\*, a starch decomposition product, etc. can be made into a carbon source, a kind AUREOBASHIDI pull lance (Aureobasidium pullulans) of black yeast can be cultivated under suitable conditions, and it can obtain as viscous polysaccharide produced in the culture medium. Although physical properties change a little with kinds of strain to be used, anything can be used for the pullulan produced by this invention.

[0022] The reaction of a raw material pullulan and a cation-ized agent is performed under existence of the specified quantity of water and the alkaline matter.

[0023] The addition of the water for a reaction is a 2 to 80 times as many mole ratio as this preferably per anhydrous glucose unit of the pullulan which is a raw material. If it is less than [ this ], since the alkaline matter which functions as a catalyst will stop participating in a reaction uniformly and the contacting efficiency of a cation-ized agent and a raw material pullulan will fall, it advances [ a reaction ] fully and is not desirable. Since there is a possibility that the reaction of the water and the cation-ized agent which are it side reaction that it is the above above-mentioned addition may advance on the other hand and the amount of deployments of a cation-ized agent falls, it is not desirable. The addition of water is a 5 to 40 times as many mole ratio per anhydrous glucose unit as this still more preferably.

[0024] If the examples of the portion (trialkylammonium base) of -NR<sub>1</sub> R<sub>2</sub> R<sub>3</sub> X common to the above-mentioned general formula (I) and (II) are enumerated in order to illustrate the cation-ized agent which can be used for this invention Trimethylammonium chloride, triethyl ammoniumchloride, TORIPURO pill ammoniumchloride etc. is begun. Dimethyl octyl ammoniumchloride, The thing containing high-class aliphatic alkyl groups, such as dimethyl desyl ammoniumchloride, dimethyl lauryl ammoniumchloride, dimethyl millimeter still ammoniumchloride, and dimethyl palmityl ammoniumchloride, etc. is mentioned.

[0025] Although the addition of the above-mentioned cation-ized agent is arbitrarily chosen by the degree of cation denaturation for which it asks, it is desirable that it is a 0.01 or more-time mole ratio per anhydrous glucose unit of a raw material pullulan. In 0.01 or less times, the degree of average substitution of the above-mentioned cation-ized pullulan per anhydrous glucose unit by the cation machine (beta-hydroxypropyl trialkylammonium base) originating in the above-mentioned cation-ized agent becomes 0.01 or less, and the target pullulan is not obtained. The mole ratio per anhydrous glucose unit is 0.1 or more still more preferably.

[0026] 40-80 degrees C of reaction temperature are desirable, and especially the addition sequence of the alkaline matter and a cation-ized agent is not limited.

[0027] After a cation-ized reaction end, after a mineral acid or an organic acid neutralizes the alkaline matter which is a catalyst, it crystallizes and collects by mixing with these mixed solvents, such as the acetone and methanol which are the non-solvent of a cation-ized pullulan, propanol, a butanol, a tetrahydrofuran, and a dioxane. The refined cation-ized pullulan can be obtained by making it dry, after remelting in underwater after an appropriate time and repeating the process of re-crystallization several times further. This is used as a basis for antistatic sizing agents for fiber.

[0028] Although sufficient effect for sizing is acquired even if it uses as 0.005 - 5.0% of the weight of solution by making only a cation-ized pullulan into a major component, the antistatic sizing agent which this invention offers is the purpose which gives the more effective antistatic effect, and can add a cation nature surfactant. The content of the cation nature surfactant in that case has 2 - 12 desirable % of the weight.

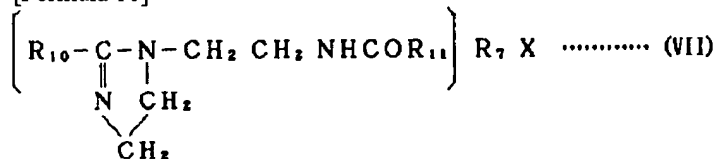
[0029] the following quarternary ammonium salt (VI) as a cation nature surfactant which can be used for this invention, imidazolinium salt (VII), the fourth class amide ammonium salt (VIII, IX, X), and cation nature polyamide (XI) etc. -- although illustrated, it is not necessarily limited to these In addition, the cation nature surfactant guided from a urea or a buret can be used.

[0030]

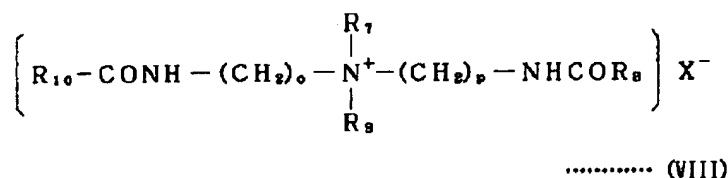
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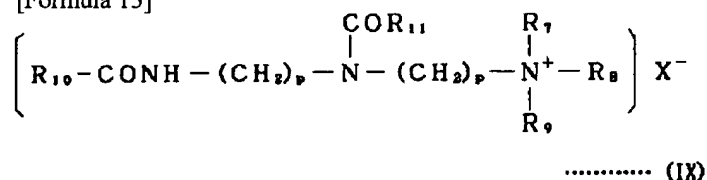
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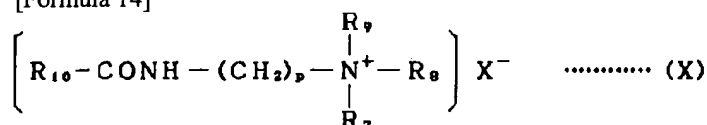
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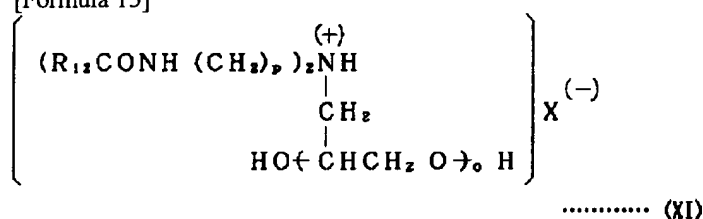
[Formula 13]



[Formula 14]



[Formula 15]



[0031] The inside R5 of the above-mentioned formula, R6, and R10 and R11 are the alkyl group of the carbon atomic numbers 11-22, or beta-hydroxyalkyl machine of the carbon atomic numbers 13-24, respectively. R7 and R8 And R9 It is the alkyl group of the carbon atomic numbers 1-3 or a hydroxyalkyl machine, a benzyl, or  $-(CH_2CH_2O)_nH$ , respectively, and R12 is the aliphatic machine of carbon numbers 12-24. 1-3p of o are 2 or 3, and X is an anion.

[0032] the more desirable cation nature surfactant which can be used for this invention -- solubility -- small -- a total carbon number -- 25-60 -- the thing of 30-50 is especially preferably good

[0033] A cation-ized pullulan is uniform, and since a film with intensity is formed, these physical properties are applicable to the sizing agent which was [ for fiber ] excellent. moreover, yellowing of fiber which was a phenomenon peculiar to a cation nature surfactant until now by using a cation-ized pullulan -- gray-ization can be prevented yellowing -- although it is not clear to a gray-ized row about the mechanism, the metal ion in tap water, colloid metallic compounds, especially iron are charged, in fiber, discoloration is brought about, because deposition is carried out [ adsorption or ], and it is thought that the cation nature surfactant is promoting this On the other hand, since a cation-ized pullulan has the work which bars adhesion for fiber by distributing the metal ion and colloid metallic compounds used as a cause, it is effective about discoloration prevention.

[0034] In addition to a cation-ized pullulan and a cation nature surfactant, the various following components can be suitably blended with the antistatic sizing agent for fiber of this invention if needed. As a combination component, antifreezing agent; perfume; germicide; antiseptics; fluorescent-dye; pigments, such as ethylene glycol, a propylene glycol, and ethanol, etc. are mentioned. In addition, nonionic surface active agents, such as a polyoxyethylene type and a polyhydric-alcohol ester type; it is also possible to blend amphoteric surface active agents, such as a betaine structured type and an imidazoline derivative.

[0035] Use of the antistatic sizing agent for fiber of this invention is possible also in any of the washing process at the time of wash, and a rinsing process, and the sizing effect and the antistatic function in which it excelled by addition of optimum dose are given. Moreover, even if the textile materials by which sizing processing was carried out with the constituent of this invention carry out several wash once processing them since film fixing is firm, an effect maintains them.

[0036]

[Example] The result is indicated to be the various examinations which followed the cation-ized pullulan used for below in examples 1-3 at the antistatic sizing agent for fiber of this invention.

[0037] Measurement of a sizing examination and deposit efficiency was performed about an example 1 cation-ized pullulan, a cation-ized cellulose, and cation-ized starch. First, the 0.4-% of the weight solution of a cation-ized pullulan (the degree 0.6 of cation substitution), a cation-ized cellulose (the degree 2.0 of hydroxyethyl substitution, the degree 0.4 of cation machine substitution), and cation-ized starch (the degree 0.5 of cation machine substitution) was prepared, respectively, and it considered as the test solution. 25g of cheesecloths was dipped in 100g of each of this test solution, and it rubbed and washed by the hand for 30 seconds. After carrying out the indirect desulfurization water of this cheesecloth for 30 seconds with a dehydrator, it dried for 5



minutes at 105 degrees C, and the heat setting of it was further carried out for 1 minute at 130 degrees C by the pin tenter. Thus, about each of the obtained examination cloth, according to JIS-1005-1959, it stretched by the cantilever method and hardness was measured. in order [ furthermore, ] to investigate about deposit efficiency -- the constant temperature of 65%RH -- it was left at 20 degrees C in the layer for 24 hours, and the weight change before and behind sizing was measured in it The result was as having been shown in Table 1. According to this, the cation-ized pullulan showed the best flare intensity and best adsorptivity.

[0038]

[Table 1]

	張り硬さ (cm)	付着率 (%)
カチオン化プルラン	6.5	91
カチオン化セルロース	5.8	82
カチオン化澱粉	5.6	79

[0039] The antistatic sex test was performed about an example 2 cation-ized pullulan, a cation-ized cellulose, and cation-ized starch. A cation-ized pullulan (the degree 0.6 of cation machine substitution), a cation-ized cellulose (the degree 2.0 of hydroxyethyl machine substitution, the degree 0.4 of cation machine substitution), and cation-ized starch (the degree 0.5 of cation machine substitution) prepared solution from which 5.0 % of the weight and a Nonion nature surfactant (polyoxyethylene alkyl ether) become 0.5% of the weight, respectively, and 0.4 % of the weight and the cation nature surfactant (JI hardening beef tallow alkyldimethyl ammoniumchloride) used these as test solution, respectively. The polyester georgette reduction finish article (075 deniers) was used for the examination cloth, and subsequent sizing processing was performed like the example 1 except for deposit-efficiency measurement. Next, with the Kyoto University-ized \*\* type rotary static circuit tester, it rubbed for 1 minute by having used \*\*\*\*\* No. 3 for the friction cloth, and band voltage was measured. The result was as having been shown in Table 2. It became clear that this has the antistatic effect excellent in the cation-ized pullulan.

[0040]

[Table 2]

	摩擦帯電圧 (V)
カチオン化プルラン	100
カチオン化セルロース	400
カチオン化澱粉	500

[0041] an example 3 cation-ized pullulan, a cation-ized cellulose, and cation-ized starch -- yellowing -- the prevention examination was performed 1g of each examination liquid prepared in the example 2 was diluted with 1000ml of tap water, and it was used as examination liquid. Subsequent sizing processing was made to be the same as that of an example 1 except for deposit-efficiency measurement at the examination cloth using the cheesecloth (92% of reflection factors) which carried out diastase processing. After repeating this sizing processing 30 times, it asked for the whiteness degree from the reflection factor of the processing cloth when making the reflection factor of a magnesium oxide into 100%, and this evaluated yellow tightness by the Elrepho (Elrepho) reflectometer (product made from curl TSUAISU). The result was as having been shown in Table 3. yellowing in which the cation-ized pullulan was excellent by this -- it became clear to have the prevention effect

[0042]

[Table 3]

	白色度 (%)
カチオン化プルラン	88
カチオン化セルロース	80
カチオン化澱粉	79

[0043] the property of have the film physical properties excellent in the cation -ized pullulan a pullulan be blend , as the antistatic sizing agent for fiber concerning this invention be showed in each above-mentioned example , and the cation machine in a molecule therefore a good sizing effect , adhesion and the further excellent antistatic effect , and yellowing -- it have a prevention effect

[0044]

[Effect of the Invention] The antistatic agent which presents the sizing effect which was excellent, without according to this invention having not made fiber discolor, but having maintained colorfastness, having excelled in the antistatic nature in low humidity, and spoiling good feeling so that clearly from the above-mentioned place can be offered.

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[Translation done.]